Report as of FY2009 for 2009PA95B: "Characterization, Treatment, and Reuse of Frac Waters related to Horizontal Hydraulic Fracturing of Marcellus Shale and Natural Gas Exploration in Pennsylvania"

Publications

Project 2009PA95B has resulted in no reported publications as of FY2009.

Report Follows

FY09 PROJECT REPORT (FINAL REPORT)
Pennsylvania Water Resources Research Center

Characterization, Geochemical Modeling, and Membrane Treatment of "Frac Water" related to Horizontal Hydraulic Fracturing of Marcellus Shale

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PRINCIPAL FINDINGS AND SIGNIFICANCE

The Marcellus Shale natural gas has the potential to develop the region's economy and improve the nation's energy independence. However, water-related issues must be considered when developing this resource. This project included chemical characterization of hydraulic fracture flowback water, geochemical modeling of flowback water changes over the duration of a fracture event, and an evaluation of membrane treatment for reducing the total dissolved solids (TDS) concentration in flowback water.

Concentrations of TDS in five collected flowback water samples ranged from three to six times (110,000 to 210,000 mg/l) saltier than sea water (35,000 mg/l) (Figure 1) and were dominated by sodium, calcium, and chloride. A review of samples from throughout the commonwealth was conducted by examining reports on file with the Department of Environmental Protection (DEP), and these files showed similar results for TDS and other parameters, although TDS concentrations varied substantially. Bromide (Br^-) concentrations in collected samples ranged from 400 to 760 mg/l, demonstrating implications for formation of brominated disinfection byproducts during potable treatment of flowback-contaminated surface waters. Barium (Ba) and strontium (Sr) concentrations were also elevated (7,600 mg/l and 3,200 mg/l, respectively) in the collected samples. In DEP files, samples fell into one of two groups: concentrations of Ba and Sr were either linearly positively correlated to TDS concentration or were unrelated, suggesting different compositions of shale brines throughout the Commonwealth, or effects of different makeup water sources for fracturing. Low-level ($\alpha+\beta$) radioactive emissions above tap water background levels were detectable in liquid scintillation counts (Figure 2), but no high-energy gamma radiation was detected.

Prior to DEP's proposed permitting strategy in 2009, it appeared that treatment of flowback water would take the form of dilution through major (>1.0 MGD) publicly-owned treatment works (POTW) effluents. Hence, a watershed analysis based on TDS was conducted (Figure 3) to determine the number of gas shale wells that could be sustained in the West Branch Susquehanna River watershed. Assumptions and results are shown in Table 1, demonstrating that dilution of flowback water TDS into ordinary municipal wastewater will support only 16 gas

shale wells per year, a number that is drastically lower than the amount of drilling anticipated in the watershed.

Table 1. West Branch Susquehanna River TDS Mass Balance Analysis.

Parameter	Assumption or Value
Background river TDS	120 mg/l, measured
Flowback water volume	1 million gallons (MG) per well, assumed
Flowback TDS	150,000 mg/l, assumed
End-of-pipe TDS standard	500 mg/l, based on DEP permitting strategy
Baseload TDS concentration in POTW effluent	350 mg/l, measured locally
Number of wells that can be supported in watershed by POTW dilution	*16 wells per year*

Geochemical models created in PHREEQC Interactive suggested that organic complexes in the oil field brine that resides in the Marcellus formation itself aid in dissolution of ions such as barium and strontium into the flowback water. While equilibria reactions in the model explained some of the observed flowback water characteristics, the controlling factor in flowback water composition was the oil field brine concentration and the ratio of mixing with the injected slickwater.

Given the high salt concentrations and DEP's proposed interim permitting strategy reducing effluent TDS to less than 500 mg/l, TDS will be the parameter governing the choice of treatment technology for this brine. Due to the dominance of monovalent ions in the flowback water, conventional chemical precipitation (via elevated pH) treatment will not reduce the TDS concentration appreciably, although precipitation of scale-prone divalent cations may become commonplace prior to reuse of flowback water. Reverse osmosis (RO) permeation tests (1,000 psig) conducted on flowback water alone yielded negligible flux through polyamide desalination membranes. However, samples received by a regional pretreatment facility are often blends of flowback water and pit water (drilling mud with lower TDS), and dilution with the pit water can result in significantly lower initial TDS concentrations (64,000 mg/l, average of two samples). Membrane treatment of these blends was more successful, with flux as high as 22 gallons per square foot per day at 800 psi transmembrane pressure. Flux was proportional to initial TDS concentration. While approximately 95% reduction in TDS was achieved (Figure 4), permeate still did not meet the PA water supply criteria of <500 mg/l TDS, suggesting that if RO or other membrane separation is to be employed, multi-stage treatment may be required.

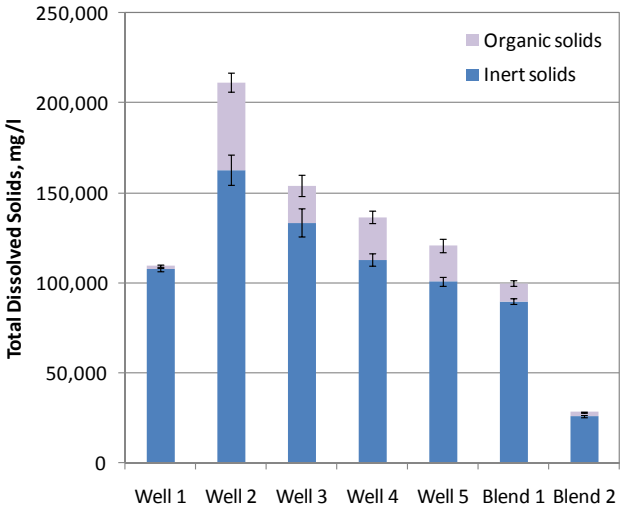

Figure 1. Flowback water TDS concentrations.

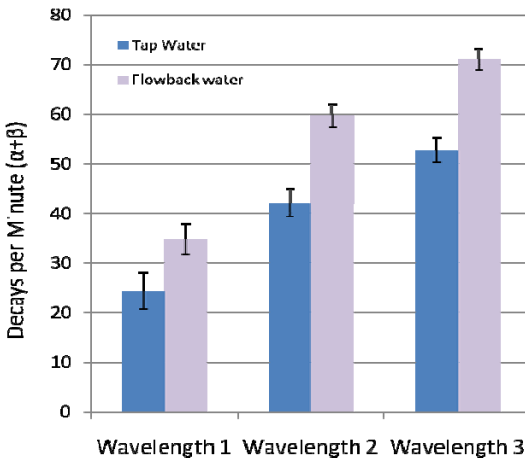

Figure 2. Flowback water radionuclides.

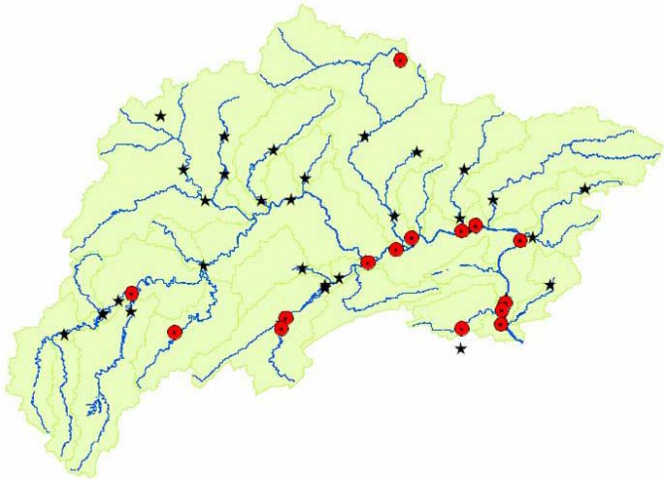

Figure 3. West Branch Susquehanna TDS Balance showing major POTWs and USGS gauging stations.

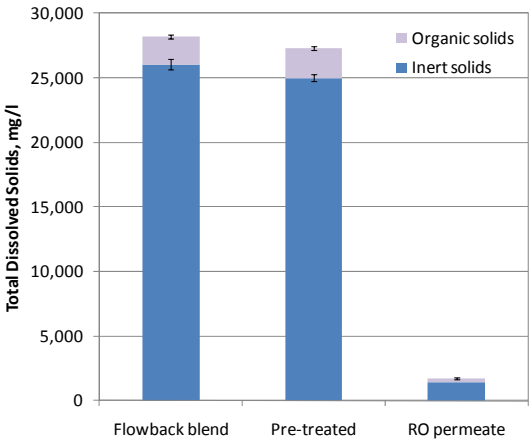

Figure 4. RO permeation of flowback-pit water blend, 800 psi, polyamide brackish desalination membrane.

STUDENTS & POSTDOCS SUPPORTED

Christopher A. Kulish, B.S. Civil Engineering, Bucknell, 2010.
Molly E. Pritz, B.S. Geology, Bucknell, 2010

PRESENTATIONS AND OTHER INFORMATION TRANSFER ACTIVITIES

Kulish, C. and K. Gilmore. (2010) Marcellus Shale natural gas wastewater characterization and treatment; Susquehanna watershed TDS analysis. Podium and poster presentations. Pennsylvania Water Environment Association (PWEA) PennTec Conference. State College, June 14-16, 2010.

Gilmore, K. (2010) Characterization, geochemical modeling, and membrane treatment of frac water. Invited presentation. PA WRRC Pennsylvania Water Symposium. State College, May 5-6, 2010.

Gilmore, K. (2010) Characterization and membrane treatment of Marcellus shale flowback water. Susquehanna River Heartland Coalition for Environmental Studies, Science of Marcellus Shale Summit. Williamsport, January 29, 2010.

Kirby, C. S. (2010) Marcellus Shale Hydrofracturing Water Geochemistry and Feasibility of Using Conductivity for Monitoring Streams, Susquehanna River Heartland Coalition for Environmental Studies, Science of Marcellus Shale Summit. Williamsport, January 29, 2010.

Kirby, C. S. (2010) Marcellus Fracwater Geochemistry and Stream Monitoring Feasibility, Marcellus Shale Natural Gas Stewardship: Understanding the Environmental Impact, *A Temple University Summit*, Philadelphia PA, April 18, 2010.

Kirby, C. S. (2010) Perspectives on Potential Environmental Impacts of Marcellus Shale Natural Gas Drilling, Bucknell Institute for Public Policy Marcellus Shale Symposium, Lewisburg PA, April 17, 2010.

Pritz, M. E. and Kirby, C. S. (2010) Geochemical investigation of Marcellus Shale natural gas hydrofracturing waters, combined annual meeting Northeastern / Southeastern Section of Geological Society of America, March 13-16, Baltimore MD.

Pritz, M. (2010) The Hydraulic Fracturing of the Marcellus Shale and Some Potential Environmental Impacts on Central Pennsylvania, presented to local League of Women Voters, Lewisburg PA, November 17, 2009

Pritz, M. (2010). Geochemical Modeling and Analysis of the Frac Water used in the Hydraulic Fracturing of the Marcellus Formation, Pennsylvania , Bucknell Institute for Public Policy Marcellus Shale Symposium, Lewisburg PA, April 17, 2010.

AWARDS

C. Kulish – Student Research Award, Pennsylvania Water Environment Association (PWEA) PennTec Conference. State College, June 14-16, 2010.

ADDITIONAL FUNDING ACQUIRED USING USGS GRANT AS SEED MONEY

None to date.

PHOTOS OF PROJECT

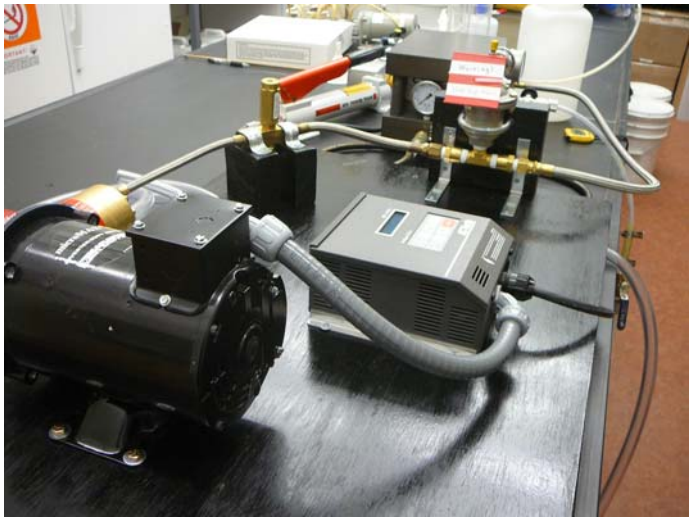

Figure 1. Lab-scale high pressure pumping system for reverse osmosis membrane treatment testing. (Photo by C. Kulish)

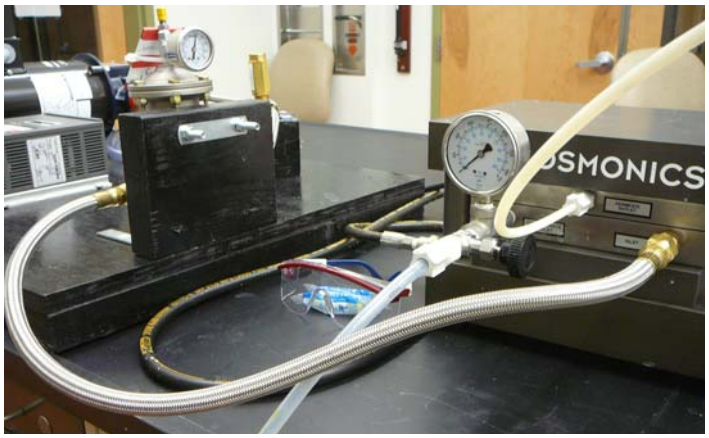

Figure 2. Lab-scale reverse osmosis membrane test apparatus. (Photo by C. Kulish)

Figure 3. Photograph illustrating residual salts remaining after sample evaporation.(Photo by K. Gilmore)